Analytical Model for SiO₂-IL Scavenging in HfO₂/SiO₂/Si Stacks Univ. of Tokyo, [°]Xiuyan Li, Takeaki Yajima, Tomonori Nishimura and Akira Toriumi E-mail: xiuyan@adam.t.u-tokyo.ac.jp

1. Introduction:

Concerning kinetics of SiO_2 interface layer (IL) scavenging in high-k gate stack [1], we have clarified both O and Si diffusion in addition to SiO_2/Si interface reaction in previous work [2-4]. This paper further proposes the analytical model of SiO_2 -IL scavenging in HfO₂/SiO₂/Si stack.

2. Results and discussion

We have described kinetics of SiO₂-IL scavenging in HfO₂/SiO₂/Si stack in UHV as that V₀ in HfO₂ moves into and reacts with SiO₂ at SiO₂/Si interface, while generated Si diffuses out through SiO₂ and HfO₂ [2-4]. Experimentally, we found that the initial scavenging and steady one were attributed to pre-existing V₀ in HfO₂ and generated V₀ in UHV, respectively. In this study, we formulate the steady scavenging by assuming i) Vo concentration in HfO₂ is constant and homogeneous, and ii) the interface reaction is in an equilibrium state as schematically shown in **Fig. 1** and in Eqs. (1)~(8). Eq. (7) is the exact formula. It includes a general parabolic form and a correction term. Note that it looks like the Deal-Grove model in Si oxidation if the correction item can be ignored. But, the coefficient in Eq. (7) is not independent but related to each other. Eq. (7) can be further simplified by assuming that Si diffusion is much slower than V₀ one as shown in Eq. (8), where *x* is proportional to *t*. **Fig. 2** demonstrates a good linear fitting between *x* and *t* on both Si and SiC substrates.

3. Conclusions

The kinetic model of SiO_2 -IL scavenging in $HfO_2/SiO_2/Si$ stack has been formulated analytically. The formula looks like Deal-Grove model but the coefficient is related to each other.

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Fig. 1 Schematics of kinetic model for formulation of SiO₂-IL scavenging in HfO₂/SiO₂/Si stack.

Fig. 2 SiO_2 -IL thickness x as function of time t in UHV annealing. x is proportional to t in steady stage.

[1] T. Ando, *Materials*, **5** (2012) 478. [2] X. Li *et al.*, IWDTF, 2013, S2-4. [3] X. Li *et al.*, SSDM, 2014, F3-3.[4] X. Li *et al.*, JSAP, 2014 autumn, 19a-A17-1.

$$F_{Vo/SiO2} = \frac{D_{Vo/SiO2}(C_{Vo/HS} - C_{Vo/int})}{x} = F_{in}, \quad (1)$$
2) At SiO₂/Si Interface reaction
 $C_{Si/int} = \kappa C_{Vo/int}^{2}, \quad (2)$
3) In Si diffusion
 $F_{Si/SiO2} = -\frac{D_{Si/SiO2}(C_{Si/HS} - C_{Si/int})}{x}, \quad (3)$
 $F_{Si/HfO2} = -\frac{D_{Si/HfO2}(C_{Si/VH} - C_{Si/HS})}{x}, \quad (4)$

 $F_{Si/VH} = K_{Si/VH}C_{Si/VH} = F_{out},$ (5) $x/L: SiO_2/HfO_2$ thickness; $D_{A/B}$: diffusion coefficient of A in oxide B; $C_{A/CD}$: Concentration of A at C/D interface; κ : equilibrium constant of SiO_2+2V_0 \leftrightarrow Si; $K_{Si/VH}$: Si desorption constant from HfO_2 to UHV. If $N_{Si}(N_{Vo})$ is the number of Si removed from (V_O incorporated into) a unit of SiO₂ layer in scavenging, $N_{Vo}=2N_{Si}$.

$$-\frac{dx}{dt} = \frac{F_{Si}}{N_{Si}} = \frac{F_{Vo}}{N_{Vo}} = \frac{F_{Vo/SiO2}}{2N_{Si}}.$$
(6)

By solving above rate equations,

$$-\frac{K_{SI/VH}C_{Vo/HS}}{N_{Si}}(t+\tau) = \frac{1}{2} \left(C_{Vo/HS}A + \frac{C}{2} \right) x^2 + \frac{B}{2} x + \frac{1}{2} \sqrt{C} \left(C_{Vo/HS}A + \frac{C}{4} \right) \cdot F(x)$$

$$A = \frac{2K_{SI/VH}}{D_{Vo/SIO2}}, B = \frac{1}{\kappa} \left(\frac{K_{SI/VH}}{D_{SI/HJO2}} L + 1 \right), C = \frac{1}{\kappa} \frac{K_{SI/VH}}{D_{SI/SIO2}}.$$

$$F(x) = \left(x + \frac{\beta}{2\alpha} \right) \sqrt{\left(x + \frac{\beta}{2\alpha} \right)^2 + \left(\gamma - \frac{\beta^2}{4\alpha^2} \right)} + \left(\gamma - \frac{\beta^2}{4\alpha^2} \right) \ln \left(\left(x + \frac{\beta}{2\alpha} \right) + \sqrt{\left(x + \frac{\beta}{2\alpha} \right)^2 + \left(\gamma - \frac{\beta^2}{4\alpha^2} \right)} \right).$$
(7)

Assuming Si diffusion is predominant and $x=x_0$ ' at t=0, there is

$$x \approx x_0' - \frac{K_{Si/VH} C_{Vo/HS}}{N_{Si} x_0 (C + 2C_{Vo/HS} A) + B} t$$
(8)